DEFENSE TECHNICAL INFORMATION CENTER

Information for the Defense Community

DTIC® has determined on ____/____/____ that this Technical Document has the Distribution Statement checked below. The current distribution for this document can be found in the DTIC® Technical Report Database.

☐ **DISTRIBUTION STATEMENT A.** Approved for public release; distribution is unlimited.

☐ **© COPYRIGHTED.** U.S. Government or Federal Rights License. All other rights and uses except those permitted by copyright law are reserved by the copyright owner.

☐ **DISTRIBUTION STATEMENT B.** Distribution authorized to U.S. Government agencies only (fill in reason) (date of determination). Other requests for this document shall be referred to (insert controlling DoD office).

☐ **DISTRIBUTION STATEMENT C.** Distribution authorized to U.S. Government Agencies and their contractors (fill in reason) (date determination). Other requests for this document shall be referred to (insert controlling DoD office).

☐ **DISTRIBUTION STATEMENT D.** Distribution authorized to the Department of Defense and U.S. DoD contractors only (fill in reason) (date of determination). Other requests shall be referred to (insert controlling DoD office).

☐ **DISTRIBUTION STATEMENT E.** Distribution authorized to DoD Components only (fill in reason) (date of determination). Other requests shall be referred to (insert controlling DoD office).

☐ **DISTRIBUTION STATEMENT F.** Further dissemination only as directed by (insert controlling DoD office) (date of determination) or higher DoD authority.

Distribution Statement F is also used when a document does not contain a distribution statement and no distribution statement can be determined.

☐ **DISTRIBUTION STATEMENT X.** Distribution authorized to U.S. Government Agencies and private individuals or enterprises eligible to obtain export-controlled technical data in accordance with DoDD 5230.25; (date of determination). DoD Controlling Office is (insert controlling DoD office).

UNIVERSITY OF DELAWARE.®

College of Engineering

HUMAN RESOURCES

Washington House
122 E. Delaware Avenue
Newark, DE 19711
Phone: 302-831-7437
Fax: 302-831-1852

July 30, 2014

Dr. Ivan Lee
U. S. Army Research Laboratory
Building 207, Room 2A26
Adelphi, MD 20783-1197

RE: Final Technical Report for W911NF-10-2-0047

Dear Dr. Lee:

Please find the enclosed final technical report on behalf of Dr. Vlachos from the University of Delaware.

Should you have technical questions regarding this report, please contact Dr. Vlachos, vlachos@udel.edu. Should you have administrative concerns, please contact Dawn Jory, dawnj@udel.edu.

Sincerely,

Michele L. Jennings

cc: Agreement Administrative Office
       Grants Officer
       Defense Technical Information Center
       CCST33211211000 File

Final Report

Development of novel catalysts for total oxidation of hydrocarbons and JP-8 at low temperature

PI: Dion Vlachos
Researcher(s): Nagesh Peela
Catalysis Center for Energy Innovation
Center for Catalytic Science and Technology
Department of Chemical and Biomolecular Engineering

Goals

The goal of this project was to develop supported bimetallic/monometallic catalysts for total oxidation of JP-8 at low temperatures. To achieve this goal, firstly catalysts for model compounds were developed using a single channel reactor, high throughput experimentation (HTE), quantum mechanical simulations, and informatics tools. Then the work was extended to more alkanes and to catalysts in a confined environment.

Overview of Achievements

We have met our aforementioned goals. The research program was founded on several main pillars discussed below.

1. Development of a High-Throughput Microreactor for Catalyst Screening and Kinetic Evaluation

In order to screen catalysts, a high-throughput reactor would significantly reduce the time for catalyst evaluation. However, one has to ensure that differences seen between microchannels are due to differences in catalysts rather than other effects, such as different flow in each channel, transport effects, etc. With this in mind, one of the earlier goals of this program was to develop the top-performing high-throughput microreactor. The design concepts were laid down in our early publication.[1]

The effect of distributor and channel positions on flow uniformity in a high-throughput reactor was studied using a COMSOL MULTIPHYSICS, CFD package. The best design was subsequently fabricated and evaluated for propane total oxidation reaction at low conversions. Comparison of our design with a literature design was also presented. The results indicate that the conical distributor performs significantly better in terms of flow uniformity as compared to the commonly used disc shaped distributor. The flow uniformity is improved when the central channel is removed from the design, indicating that the channel arrangement also affects the flow uniformity. The experimental results on flow uniformity
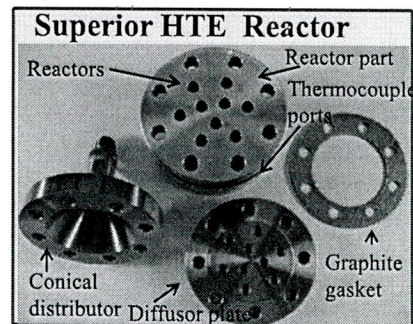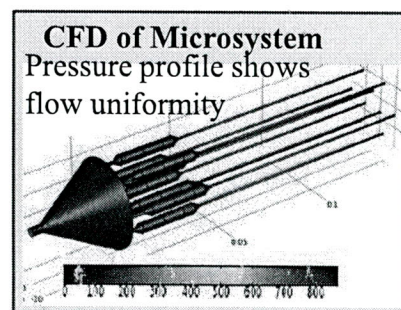

Figure 1: CFD simulation (top) used to optimize the high throughput microreactor and picture of the fabricated microreactor (bottom).

1

are in good agreement with simulation. The deviation in conversion of propane from channel to channel is within experimental error, indicating that the reactor can reliably screen catalysts and deliver kinetics. Several catalysts were tested for complete propane oxidation using the developed technology.

2. Development of Detailed Kinetic Models for Total Oxidation of Hydrocarbons

Our ability to understand and eventually predict oxidation of JP-8 on catalysts is severely limited by the lack of detailed, reliable kinetic models. This shortcoming also undercuts our ability to develop superior catalysts for catalytic combustion. Prior to our work, associated models for hydrocarbons larger than methane were rather empirical.

In this work, a microkinetic model was developed for ethane total oxidation, under fuel-lean conditions on a Pt catalyst using input from density functional theory and Brønsted-Evans-Polanyi linear free energy relations. Our choice of ethane is that it is the smallest paraffin where in addition to C-H bond cleavage, C-C bond scission much also occur. This diversity in bond breaking can change the important reaction step compared to methane. The results were published in the Ind. Eng. Chem. Res.[2]
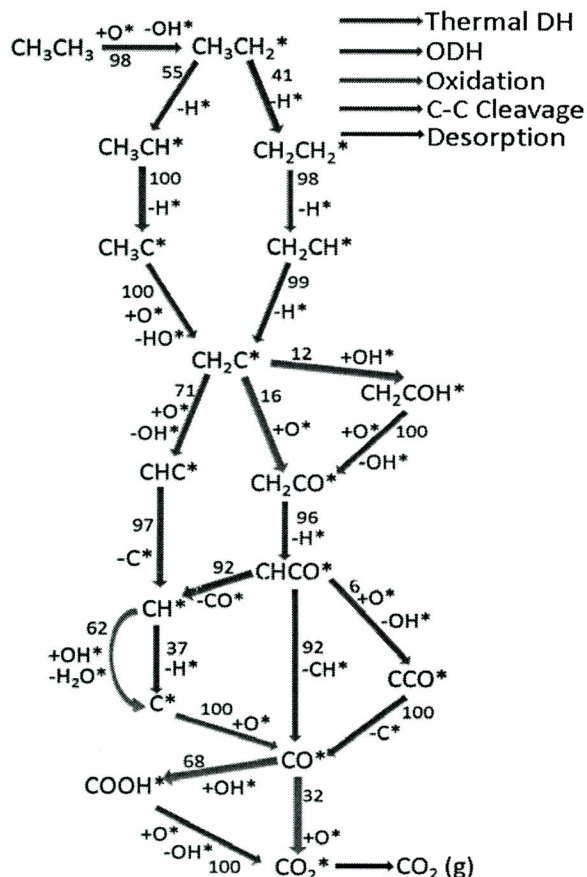
Figure 2: Reaction mechanism predicted from the microkinetic model (with O* coverage effects on barriers). The numbers on the arrows indicate the percentage of reactant converted via that pathway.

Reaction orders and the apparent activation energy estimated from the model were in good agreement with experimental values obtained in our laboratory. The inclusion of oxygen coverage effects on the activation of ethane changes the rate-determining step from thermal dehydrogenation to oxidative dehydrogenation of ethane where O-assisted removal of H controls the rate. So we have shown for the first time that including coverage effects in total oxidation is important. We have found that significant portion (30%) of the reaction flux proceeds via oxygen insertion reactions to C_2 hydrocarbons (CH$_2$C*), something that has not been anticipated or proposed earlier (see Figure 2).

Our results provide clear take-home messages. First, they show that ethane, despite being a larger hydrocarbon and exhibiting C-H and C-C bond scissions, has the same rate-determining step with methane. Thus, our findings strongly support the concept of a homologous series where hydrocarbon activation is the most kinetically relevant step. Second, aside from the carbon, C, binding energy, the oxygen, O, binding energy may also be important in finding better catalysts. We explore this in the next pillar of our work.

2

3. Development of Superior Catalysts for Total Oxidation of Hydrocarbons

Despite significant research efforts, predicting bimetallic catalysts with superior performance rationally remains a challenging task. In this study, we combined the strengths of high throughput experiments, density functional theory calculations, and simple informatics tools (see Figure 4) synergistically for predicting novel core-shell catalyst structures of bimetallics. In addition the catalyst stability was considered. We have combined insights from the modeling studies in Task 2 with density functional theory to down select catalysts that are both active and selective. Propane total oxidation was employed as a probe, proof-of-concept reaction. The results were published in the high impact ChemCatChem journal and the article was featured in the cover of the journal (Figure 3).[3]

The methodology we developed is successful in predicting three bimetallic catalysts. Among them, Ag-Pd is cheaper, more active than the existing most active single metal catalyst (Pt), and stable at reaction conditions (see Figure 5). Extended X-ray Absorption Fine Structure characterization confirms the formation of bimetallic alloy. This study provides a path forward for designing bimetallic catalysts rationally for vapor phase metal catalyzed reactions. One question is whether the studies on small hydrocarbons we focused on are relevant for JP-8. We believe that this is indeed the case. This was addressed above in Task 2 based on modeling results. We provide further experimental evidence next (Task 4).
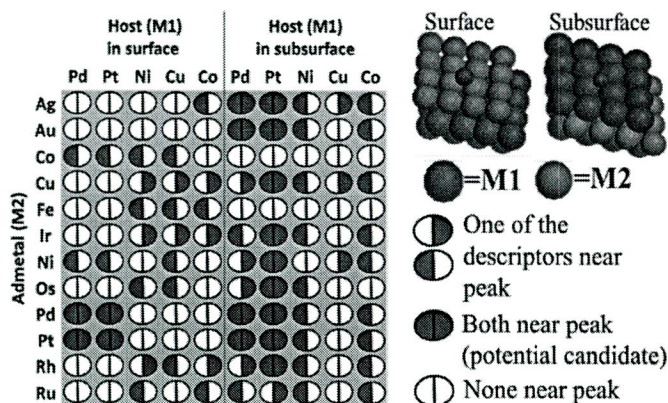

Figure 4: Computational screening results to identify potential bimetallic structures for propane total oxidation reaction. The left half-red ellipses indicate bimetallics with C binding energy near the peak and the right half-red ellipses indicate bimetallics with the O binding energy near the peak of the activity map. These results have been used to select a small number of potentially very active catalysts.
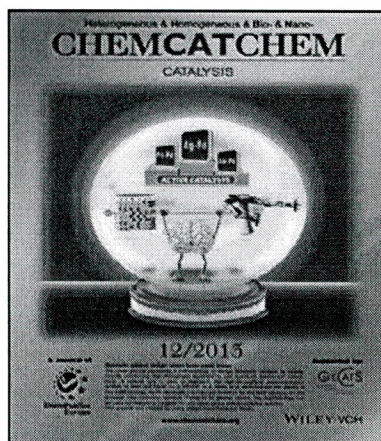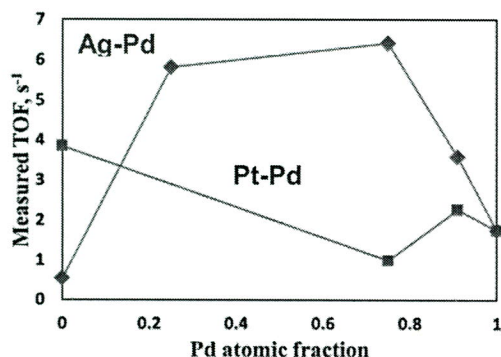

Figure 3: Journal cover of our publication.

Figure 5: Propane turnover frequency as a function of Pd atomic fraction in bimetallic catalysts Ag-Pd/Al_2O_3 and Pt-Pd/Al_2O_3. Lines are drawn to guide the eye.

4. Homologous Series Experiments

A volcano type relation has been found between turnover frequency (TOF) of total oxidation of propane and atomic carbon and oxygen binding energies in our previous study (Task 3). The objective of this study is to explore the hypothesis that there is a correlation among the oxidation chemistry of hydrocarbons in a homologous series and the results can be applied to dodecane, the major component of JP-8. Experimental volcano curves are constructed for small hydrocarbons to test this hypothesis. The results will be published in a future communication.

We tested 7 single metal catalysts for the total oxidation of small hydrocarbons (methane, ethane, propane, and isobutene using our high throughput reactor system described above. The TOF of various hydrocarbons at 300 °C as a function of carbon binding energy is plotted in Figure 6. The conversion was maintained below 20% to ensure operation in the kinetic regime. The TOF for all hydrocarbons tested follows a volcano type relation with respect to the carbon binding energy. The optimal carbon binding energy required for this reaction is approximately constant and slightly lower only for isobutane. The TOF changes with carbon number as shown for Pt/Al_2O_3 and Pd/Al_2O_3 in 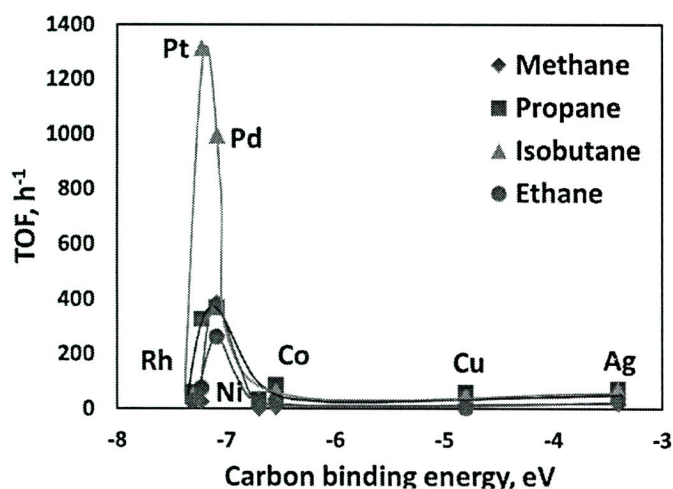Figure 6. The TOF on Pt is very low for small hydrocarbons as compared that on Pd catalyst. However, as the carbon number increases, the activity on Pt increases at a faster rate than that on Pd and the activity trend reverses for isobutane. This indicates that larger hydrocarbons require stronger binding energy to obtain higher activity. The reasons for this trend are not quite clear at this point. One reason postulated in the literature is that the Pt has a maximum pre-exponential at propane whereas the pre-exponential of Pd monotonically decreases with carbon number.[4] Our data is consistent with the fact that the experimental desorption energies of hydrocarbons on Pt(111) increase with increasing carbon number.[5]

Figure 6: Turnover frequency of conversion of various hydrocarbons as a function of Carbon binding energy.

In conclusion, a volcano type relation is observed with all the hydrocarbons tested. The carbon binding energy is approximately fixed indicating that the best catalyst descriptors remain approximately fixed for the entire homologous series.

5. Metal Encapsulated Zeolite Catalysts

In the quest for more active catalysts, we have explored the effect of confinement. Several metal encapsulated zeolite catalysts, synthesized using various methods, were tested for propane total oxidation reaction. The results will be published in future communication.

Figure 7 shows the conversion of propane as a function of temperature, for the catalysts which show higher activity than that of $1\%Pt/Al_2O_3$ catalyst. The zeolite catalysts synthesized by hydrothermal method and whose silica to alumina ratio is ∞ are not as active as the $1\%Pt/Al_2O_3$ catalyst. The reason for this lower activity are currently unclear. Yazawa et al.[6] found that the activity of supported Pt catalysts increase with acidic strength of the support. The major reason for this effect is the improvement of oxidation-resistance of Pt with acidic supports. The dependence

of activity on acid strength support also depends on the metal. For example if the metal in the supported metal catalysts is Pd, then supports with moderate acid strength give higher activity.[7] This could be due to the fact that the less oxidized Pt is good for this reaction whereas Pd should be in partially oxidized state to obtain high activity. Therefore, the metal-support interactions play an important role. The zeolite catalysts synthesized by metal complex incorporation are also not active. The zeolite catalysts synthesized by ion-exchange method are highly active and the activity is much higher than that of Pt/Al_2O_3 catalyst.

Based on this data, we short-listed four ion-exchanged zeolite catalysts to study further. We used very low weight fraction of Pt (~0.1%) to avoid light-off conditions. Figure 7 shows the conversion of propane with temperature along with that on Pt/Al_2O_3 for comparison. Even though, the amount of platinum in the metal encapsulated zeolites is very low as compared that of $1\%Pt/Al_2O_3$, the conversion on zeolite catalysts is much higher compared to that on Pt/Al_2O_3. The TOF with all the zeolite catalysts is very high as compared to that on $1\%Pt/Al_2O_3$ catalyst. The rate on Pt/Beta with silica to alumina ratio of 25 is the highest and is at least two orders of magnitude higher than that on $1\%Pt/Al_2O_3$ catalyst. The higher rate on zeolite catalysts could be attributed to higher propane uptake by zeolite catalysts.[8] Other reasons for this higher activity could be metal-support interactions which could modify the electronic and geometric properties of metals inside the zeolite pores. Confirmation of such properties require further study using advanced characterization techniques such as in-situ FTIR of adsorbed CO, EXAFS and XPS.
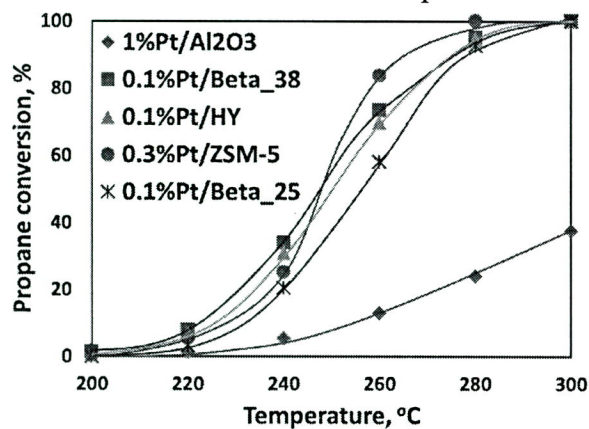

Figure 7: Propane conversion as a function of temperature on short-listed metal encapsulated zeolite catalysts (see Table 3). Pt/Al_2O_3 is also included for comparison.

Publications Resulting From This Program

1. Peela, N. R.; Lee, I. C.; Vlachos, D. G., Design and Fabrication of a High-Throughput Microreactor and Its Evaluation for Highly Exothermic Reactions. *Ind. Eng. Chem. Res.* **2012,** *51* (50), 16270-16277.
2. Peela, N. R.; Sutton, J. E.; Lee, I. C.; Vlachos, D. G., Microkinetic Modeling of Ethane Total Oxidation on Pt. *Ind. Eng. Chem. Res.* **2014,** *53* (24), 10051-10058.
3. Peela, N. R.; Zheng, W.; Lee, I. C.; Karim, A. M.; Vlachos, D. G., Core–Shell Nanocatalyst Design by Combining High-Throughput Experiments and First-Principles Simulations. *ChemCatChem* **2013,** *5* (12), 3712-3718.
4. Peela, N. R.; Lee, I. C.; Vlachos, D. G., Design Principles for Homologous Series of Fuels: Application to Alkanes, Combust. Flame, In preparation.
5. Peela, N. R.; Lee, I. C.; Lobo, R.F., Vlachos, D. G., Metal encapsulated zeolite catalysts enhance performance significantly over noble metals supported on g-alumina, To be communicated.

References

1. Peela, N. R.; Lee, I. C.; Vlachos, D. G., Design and Fabrication of a High-Throughput Microreactor and Its Evaluation for Highly Exothermic Reactions. *Ind. Eng. Chem. Res.* **2012,** *51* (50), 16270-16277.
2. Peela, N. R.; Sutton, J. E.; Lee, I. C.; Vlachos, D. G., Microkinetic Modeling of Ethane Total Oxidation on Pt. *Ind. Eng. Chem. Res.* **2014,** *53* (24), 10051-10058.
3. Peela, N. R.; Zheng, W.; Lee, I. C.; Karim, A. M.; Vlachos, D. G., Core–Shell Nanocatalyst Design by Combining High-Throughput Experiments and First-Principles Simulations. *ChemCatChem* **2013,** *5* (12), 3712-3718.
4. Aryafar, M.; Zaera, F., Kinetic study of the catalytic oxidation of alkanes over nickel, palladium, and platinum foils. *Catalysis Letters* **1997,** *48* (3-4), 173-183.
5. Tait, S. L.; Dohnálek, Z.; Campbell, C. T.; Kay, B. D., n-alkanes on Pt(111) and on C(0001)/Pt(111): Chain length dependence of kinetic desorption parameters. *The Journal of Chemical Physics* **2006,** *125* (23), -.
6. Yazawa, Y.; Yoshida, H.; Hattori, T., The support effect on platinum catalyst under oxidizing atmosphere: improvement in the oxidation-resistance of platinum by the electrophilic property of support materials. *Applied Catalysis A: General* **2002,** *237* (1–2), 139-148.
7. Yazawa, Y.; Yoshida, H.; Takagi, N.; Komai, S.-i.; Satsuma, A.; Hattori, T., Acid Strength of Support Materials as a Factor Controlling Oxidation State of Palladium Catalyst for Propane Combustion. *Journal of Catalysis* **1999,** *187* (1), 15-23.
8. Garetto, T. F.; Rincón, E.; Apesteguía, C. R., The origin of the enhanced activity of Pt/zeolites for combustion of C2–C4 alkanes. *Applied Catalysis B: Environmental* **2007,** *73* (1–2), 65-72.